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| (74) Agent: COHEN, Alan, Nicol; 2 Grove Place, Tatsfield, Westerham, Kent TN16 2BB (GB). | | Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> |

(54) Title: **MEMBRANE PRE-TREATMENT PROCESS**

(57) Abstract

An improved porous substrate for zeolite membranes is formed by coating the substrate with a layer of zeolite particles of a narrow particle distribution size of between 20 and 0.01 microns.

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Membrane Pre-Treatment Process

The present invention relates to a method for forming inorganic membranes, more particularly it relates to a method for forming zeolite membranes.

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It is known to form zeolite membranes by crystallisation of zeolites from gel solution onto a substrate such as a metal mesh substrate or a porous ceramic substrate. The membranes which can be used in the present invention can be formed by any method, for example by crystallisation from a gel or solution, by plasma deposition or by any 10 other method such as electro-deposition of crystals on conducting substrates e.g. as described in DE 4109037.

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When the membrane comprising a film of zeo-type material is prepared by crystallisation from a synthesis gel, any of the methods described in the prior art can 15 be used for example, as described in EP-A-57049, EP-A-104800, EP-A-2899 and EP-A-2900. Standard text books by D W Breck ("Zeolites Molecular Sieves, Structure Chemistry and Use") published by John Wiley (1974) and P.A Jacobs and J.A Martens (Studies in Surface Science and Catalysis No. 33, Synthesis of High Silica 20 Alumino silicate Zeolites" published by Elsevier (1987), describe many such synthesis gels. The process which can be used includes conventional syntheses of zeo-type materials, except that the synthesis is carried out in the presence of the porous support. Most commonly, gels are crystallised by the application of heat.

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Preferred methods are disclosed in our copending patent applications 25 PCT/GB96/00243, PCT/GB97/00928 and PCT/GB 97/00635.

It is known to pre-treat the substrate before deposition of the zeolite onto the mesh e.g. as described in patent application US 5,716,527.

We have now discovered a method of pre-treating a porous substrate to give an improved membrane.

According to the invention there is provided a method of treating a porous substrate 5 which method comprises passing a suspension of zeolite particles in a liquid suspension through the porous support until a coating of zeolite particles is formed on the support surface and in which the particles have a diameter of between 20 μ m and 0.1 μ m.

10 We have found that a narrow size range of zeolite particles gives unexpectedly superior results.

15 Preferably the range of particles is achieved by mixing together particles of different size distribution. Zeolite particles, when prepared will have a particle size distribution, if these particles are ground or pulverised the average size is reduced and the distribution of sizes changed. If these particles are mixed with the unground particles a mixture can be obtained with a preferred size distribution for use in the present invention.

20 Preferably the zeolite particles are a mixture of particles which conforms approximately to a modified Fuller curve.

Fuller curves are grading curves which give the minimum void space and closest packing for sands and other mineral aggregates containing particles of varying sizes.

25 The shape of the Fuller curve will depend on the maximum particle size, but will be a single curve for any given maximum particle size.

The Fuller curves are described in a paper by Fuller and Thomson entitled "The laws of Proportioning Concrete" published in the Transactions of the American Society of

30 Civil Engineers. 1907, 59, pages 67-172. The Fuller curves are identified by their

maximum particle size. e.g. in the present invention a preferred particle distribution is a 20 μ m Fuller curve.

5 The porous supports on which zeo-type membranes are formed and which can be used in the present invention include those formed of metals, ceramics, glass, mineral, carbon or polymer fibres or cellulosic or organic or inorganic polymers. Suitable metals include titanium, chromium and alloys such as those sold under the Trade Marks "Fecralloy" and "Hastalloy" and stainless steels. The porous supports may be formed of a mesh or from sintered metal particles or a mixture of both. These are 10 commonly sold in the form of filters.

15 Porous ceramics such as glass mineral or carbon materials are preferred including alumina, porous silicon and other carbides, clays and other silicates and porous silica. If desired, the support can be a zeolite formed by compression or using a binder. The shape of the support is not critical, for example, flat sheet, tubular, wound spiral, etc. can be used.

20 The porous support can be also be a granular solid e.g. formed of particles of a closely packed material such as a pellitised catalyst.

25 The present invention can be used with porous supports of any suitable size although, for large flux rates through a membrane, large pore sizes are preferred. Preferably pore sizes of 0.01 to 2,000 microns, more preferably of 0.1 to 200 and ideally of 0.1 to 20 microns are used. Pore sizes up to 300 microns can be determined by bubble point pressure as specified in ISO 4003. Larger pore sizes can be measured by microscopic methods.

30 The method of the present invention is particularly useful for forming a zeolite membrane on the inside of a tubular porous support e.g. in a ceramic monolith.

In this application of the method of the invention a suspension of the zeolite particles is passed through the bore of the tube and out through the walls of the tube so as to deposit a layer of zeolite membranes on the inner surface of the tube.

5 The process is continued until the desired thickness of particles are deposited on the inner surface or a pre-determined flux of the liquid passes through the tube walls.

The suspension of zeolite particles is preferably an aqueous suspension of the particles and the suspension can be formed by forming a mixture of zeolite particles

10 and water and grinding this mixture in a grinder until the particles are of the requisite size for use in the invention. The particles can be ground or milled in a conventional grinder or mill. Alternatively the particles can be reduced in size by a combination of shear, cavitation and impact e.g. as occurs in a microniser. These ground particles can be mixed with particles of a larger size so that the required particle size distribution is 15 obtained.

After treatment a zeolite membrane can be formed on the treated substrate by any of the methods described in the prior art referred to above and the method is particularly useful when the membrane is formed by gel crystallisation.

20 The invention is described in the following example

Example

25 The apparatus shown in Figure 1 was used to deposit the zeolite particles, this apparatus consists of a reservoir vessel (3) connected via a circulating pump (2) capable of achieving flow rates of 16 l/min and a pressure of 35 psi. to the tubular membrane (8) which is held in an appropriate housing (1). The feed outlet is connected back to the reservoir vessel via a pressure gauge (4) and an adjustable valve (5) capable of totally restricting the feed flow. The permeate outlet (7) from the

30

housing is also connected to the reservoir vessel via flexible tubing that allows samples of permeate flow to be taken over timed intervals. The temperature is monitored by temperature gauge (6).

5 The following method is used to deposit the zeolite crystals.

To 7 litres of distilled, deionised water are added 30g of standard zeolite 4A particles having an overall particle size distribution between 20 μm and 0.1 μm as shown in Figure 2 and 3g of zeolite 4A particles that have been micronised to an overall size 10 range between 20 and 0.1 μm , as shown in Figure 3 as measured by a Fritsch Particle Size Analyser Model 22. The particle distribution before micronisation is shown in Table 1 and the particle distribution after micronisation is shown in Table 2 respectively.

15

Table 1 **Particle size before micronisation (volume %)**

| | | | |
|------------|----------------------|---------|-----------------------|
| 00.50 % | < 0.20 μm | 00.90 % | < 0.24 μm |
| 03.32 % | < 0.43 μm | 04.30 % | < 0.49 μm |
| 20 05.00 % | < 0.53 μm | 10.00 % | < 0.77 μm |
| 15.00 % | < 1.02 μm | 20.00 % | < 1.33 μm |
| 30.00 % | < 2.16 μm | 40.00 % | < 3.15 μm |
| 50.00 % | < 4.05 μm | 60.00 % | < 4.88 μm |
| 70.00 % | < 5.75 μm | 80.00 % | < 6.75 μm |
| 25 90.00 % | < 8.29 μm | 99.00 % | < 12.62 μm |

Table 2 Particle Size after micronisation (volume %)**Interpolation Values**

| | | | |
|------------|----------------------|---------|----------------------|
| 00.50 % | < 0.17 μm | 00.90 % | < 0.19 μm |
| 03.32 % | < 0.30 μm | 04.30 % | < 0.34 μm |
| 5 05.00 % | < 0.37 μm | 10.00 % | < 0.53 μm |
| 15.00 % | < 0.66 μm | 20.00 % | < 0.79 μm |
| 30.00 % | < 1.05 μm | 40.00 % | < 1.35 μm |
| 50.00 % | < 1.69 μm | 60.00 % | < 2.05 μm |
| 70.00 % | < 2.47 μm | 80.00 % | < 2.97 μm |
| 10 90.00 % | < 3.69 μm | 99.00 % | < 5.64 μm |

This suspension is circulated around the system under crossflow conditions for 1 minute (valve (5) fully open). Permeate is collected after this time for 30 seconds and weighed prior to returning it to the main reservoir. Valve (5) is fully closed for 1 minute to ensure all the flow passes through the walls of the porous support. Again the permeate is collected for 30 seconds, weighed and returned to the reservoir valve (5) is then fully opened for 1 minute.

This procedure of opening and closing the valve (5) is continued until the target flux through the porous medium is reached. For example for an alpha alumina porous substrate with a pore size range between 4.5 and 1.3, the target permeate flux is < 50 cm^3 per minute in dead end flow conditions.

The tube is removed from the apparatus, allowed to dry at 70°C for 3-4 hours

25 The zeolite membrane was formed on the inside of the support pre-treated with the particles by allowing a hydrogel suspension to be in contact with the surfaces under the conditions described below.

The hydrogel is formed by combining two separate solutions, (solution A) and (solution B) to form a homogeneous suspension.

Solution A

5

24.49g Sodium Aluminate, 3.75g Sodium Hydroxide and 179.74g de-ionised water were mechanically shaken until dissolved. The Sodium Aluminate had an actual composition 62.48% Al₂O₃, 35.24% Na₂O, and 2.28% H₂O.

10 Solution B

50.57g Sodium Silicate of composition 14.21% Na₂O, 35.59% SiO₂ and 50.20% H₂O was dissolved in 148.8g de-ionised water.

15 Solution A was heated to 50⁰C and added slowly to solution B which had been pre-heated to 90⁰C with stirring to ensure complete and even mixing (it is important that no lumps of hydrogel are formed). The mixture was then heated to 95⁰C. This resulted in a hydrogel having a molar composition

20 2.01 Na₂O : Al₂O₃: 2.0 SiO₂ : 143.10 H₂O

25 The pre-treated tube was wetted by immersing it in deionised water for 15 seconds. The tube was then suspended vertically above the bottom of the growth vessel. Hot hydrogel was then added to the growth vessel, care being taken to ensure that all the air was expelled from the inside of the support.

The growth vessel was sealed and heated to 100⁰C for 5 hours.

After 5 hours the tube was removed from the growth vessel, allowed to cool slightly and then removed and washed clean using deionised water over a period of 16 hours. The ceramic tube was then dried at 100°C for 6 hours.

5 X-ray Analysis showed this to be a Zeolite 4A.

A mixture of polysilicic acids of mean molecular weight of about 800 was diluted with ethanol to 5% wt. solids. 500ml. of this solution was circulated over the feed side of the membrane and drawn through the membrane to treat the surface whilst 10 being heated to 70° C., with vacuum for 5 hours to cross-link the silicic acid in the pores of the membrane.

The tubes were pre-treated with various particles and a zeolite membrane formed on the inner surface of the coated tubes as described above and the results described 15 below.

In run 1 the pre-treatment used the mixture of particles formed as described in Example 1, with properties as described in Tables 1 and 2 above, followed by one zeolite growth.

20

In run 2 the pre-treatment used particles of Table 1 only followed by two zeolite crystal growths.

When only micronised particles of Table 2 were used it was not possible to form a 25 vacuum.

The results for Runs 1 and 2 are shown below in Table 3.

Table 3

| | | <u>Run 1</u> | <u>Run 2</u> |
|-----------|--|--------------|--------------|
| 5 | | | |
| | Tube weight clean (grms) | 298.43 | 298.83 |
| | Tube vacuum (mbar) | 0.786 | 0.7895 |
| | Tube weight after pre-treatment (grms) | 298.47 | 307.69 |
| | Increase in weight (grms) | 0.04 | 8.86 |
| 10 | Tube vacuum after pre-treatment | 0.7202 | 0.69 |
| | Weight after crystal growth | 299.79 | 304.14 |
| | Increase in weight | 1.36 | - 3.55 |
| | Tube vacuum after growth | 0.0088 | 0.2144 |

15 2nd Growth

| | |
|-----------------------------|--------|
| Weight after crystal growth | 305.76 |
| Increase in weight | 1.62 |
| Tube vacuum after growth | 0.045 |

20

The flux characteristics for Run 1 are shown in Fig 4 and the flux characteristics for Run 2 are shown in Table 5.

The performance of the membrane formed in Run 1 are given below in Table 4

25

Table 4

| | Feed 5 | Permeate %/w/w | Total Flux g/h | Water Flux g/h | Water Flux kg/m ² /d | Solvent Flux kg/m ² /d | Time hrs. |
|--|-----------|-------------------|-------------------|-------------------|------------------------------------|--------------------------------------|--------------|
| | 3.32 | 99.17 | 34.438 | 34.152 | 17.59 | 0.15 | 0.5 |
| | 1.75 | 96.9 | 21.778 | 21.103 | 10.87 | 0.35 | 0.5 |
| | 0.91 | 88.15 | 10.258 | 9.042 | 4.66 | 0.63 | 0.5 |
| | 0.44 | 68.61 | 8.196 | 5.623 | 2.90 | 1.32 | 0.6 |

10

Table 5

| | Feed 15 | Permeate %/w/w | Total Flux g/h | Water Flux g/h | Water Flux kg/m ² /d | Solvent Flux. kg/m ² /d | Time. hrs. | Cum.Time hrs. |
|--|------------|-------------------|-------------------|-------------------|------------------------------------|---------------------------------------|---------------|------------------|
| | | | 0.000 | 0.00 | 0.00 | 0.00 | 0.0 | 0.0 |
| | 3.99 | 99.34 | 31.640 | 31.431 | 15.62 | 0.10 | 0.5 | 0.5 |
| | 2.55 | 98.48 | 22.32 | 21.894 | 10.88 | 0.17 | 0.5 | 1.0 |
| | 1.55 | 94.23 | 14.618 | 13.775 | 6.85 | 0.42 | 0.5 | 1.5 |
| | 0.94 | 83.74 | 9.760 | 8.173 | 4.06 | 0.79 | 0.5 | 2.0 |
| | 0.58 | 62.68 | 7.668 | 4.730 | 2.35 | 1.46 | 0.5 | 2.5 |
| | 0.36 | 35.08 | 7.390 | 2.592 | 1.29 | 2.38 | 0.5 | 3.0 |

As can be seen the mixture of particles of a range of sizes gives superior results.

25

Claims

1. A method of treating a porous substrate which method comprises passing a suspension of zeolite particles in a liquid suspension through the porous support until a coating of zeolite particles is formed on the support surface and in which the particles have a diameter of between 20 μ m and 0.1 μ m.

5 2. A method as claimed in claim 1 in which the zeolite particles have a range of sizes and are formed by mixing together particles of different size distribution.

10 3. A method as claimed in claim 2 in which ground zeolite particles are pulverised and are mixed with the unground particles.

15 4. A method as claimed in claim 1 or 2 in which the zeolite particles are a mixture of particles which conforms approximately to a modified Fuller curve.

5 5. A method as claimed in any one of claims 1 to 4 in which the porous substrate is formed of a metal, ceramic, glass, mineral, carbon or polymer fibres or cellulosic or organic or inorganic polymers.

20 6. A method as claimed in claim 5 in which the porous substrate is formed of a mesh or from sintered metal particles or a mixture of both.

25 7. A method as claimed in claim 4 in which the porous substrate is an alumina, carbide, clay, silicate, silicon carbide or a porous silica.

8. A method as claimed in claim 6 in which the porous substrate is a granular solid formed of particles of a closely packed material.

30 9. A method as claimed in any one of the preceding claims in which the porous

support has a pore size of 0.01 to 2,000 microns.

10. A method as claimed in any one of the preceding claims in which the porous support has a pore size of 0.1 to 20 microns.

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11. A method as claimed in any one of the preceding claims in which the porous substrate has tubular conduits formed within it and a suspension of the zeolite particles is passed down through the tubular conduits and out through the walls of the tubular conduits so as to deposit a layer of zeolite particles on the inner surface of the

10 tubular conduits.

12. A method as claimed in claim 11 in which the suspension of zeolite particles is formed by forming a mixture of zeolite particles and water and grinding this mixture in a grinder until the particles are of the requisite size.

15

13. A porous substrate having a coating of zeolite particles formed on it by the method of any one of claims 1 to 12.

14. A porous substrate as claimed in claim 13 in which there is a zeolite membrane
20 formed on the substrate.

15. A porous substrate as claimed in claim 14 in which the membrane is formed by gel crystallisation.

25 16. A porous substrate formed from a ceramic monolith in which there are tubular conduits formed on the inside of the ceramic monolith and in which there is a coating of zeolite particles formed on the inside walls of the tubular conduits according to the method of any one of claims 1 to 12 and in which a zeolite membrane is formed on the coated walls.

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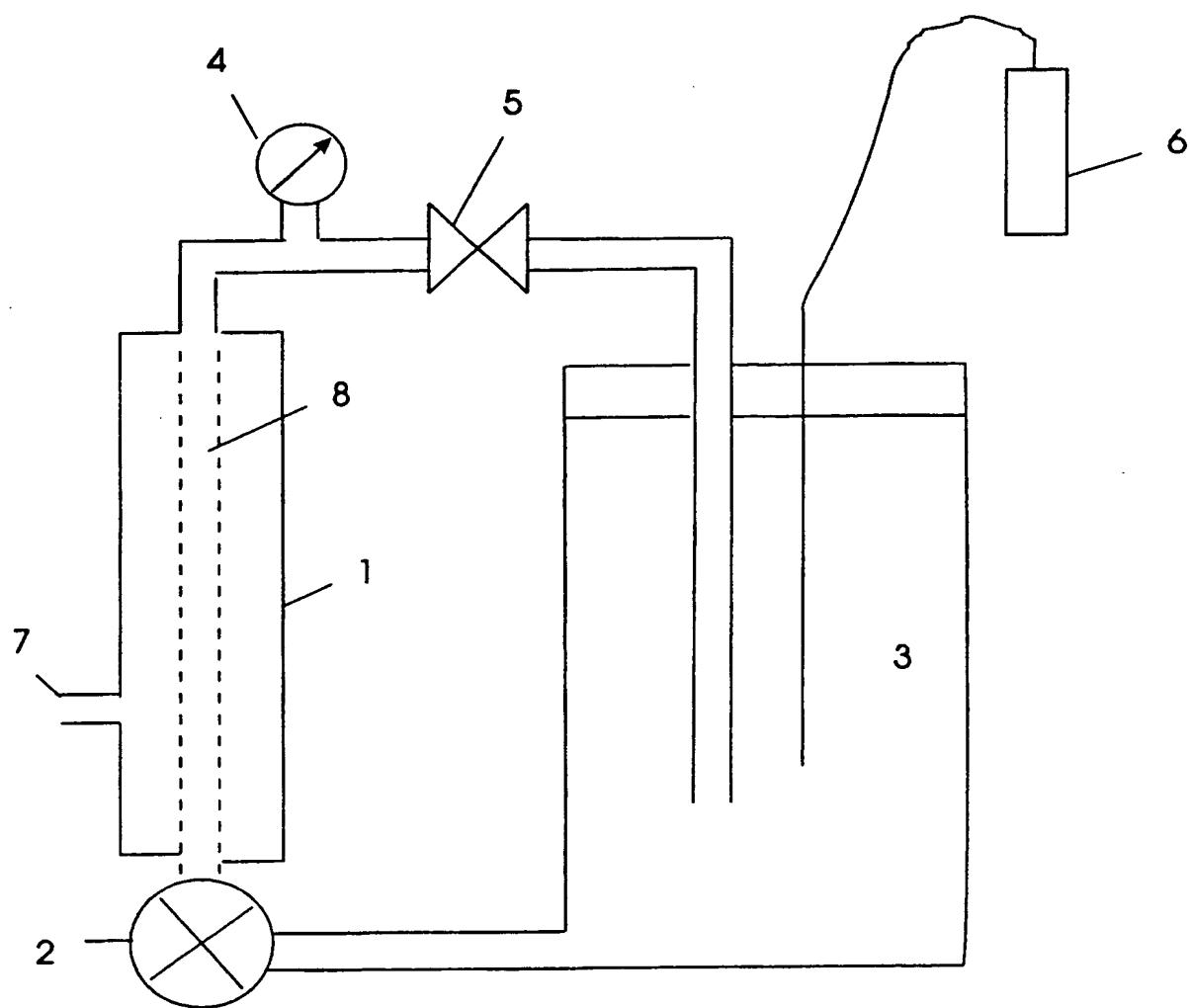
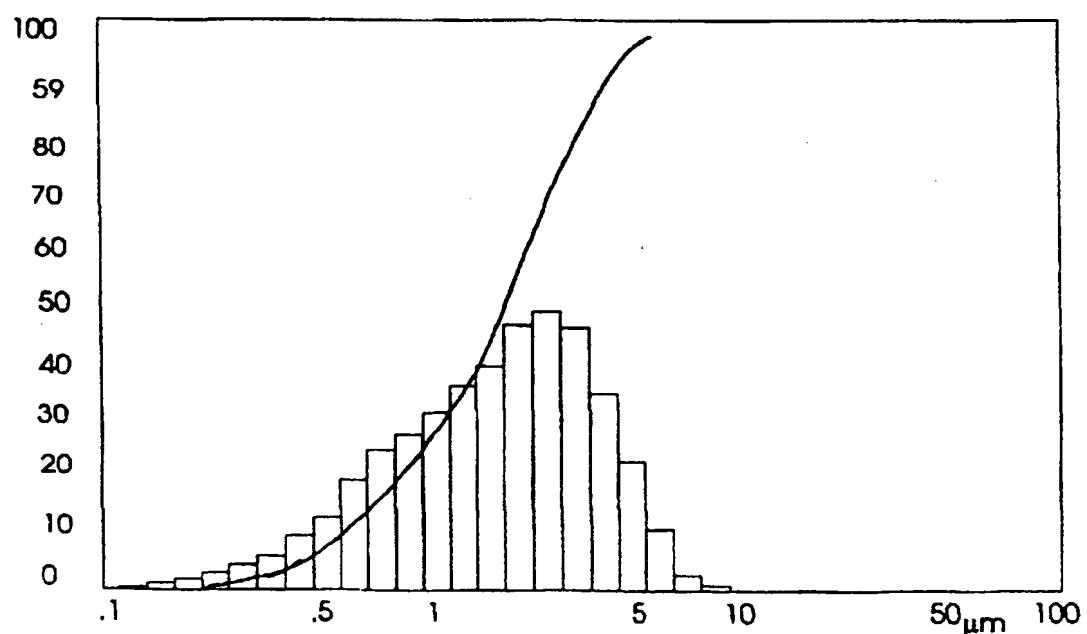


Fig. 1

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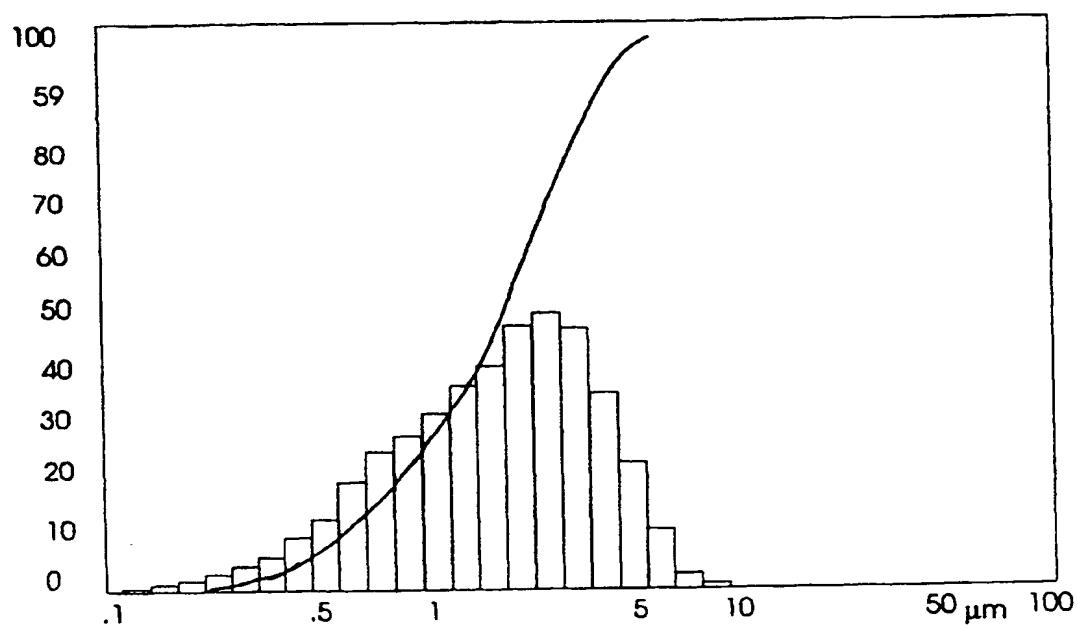


Fig. 3

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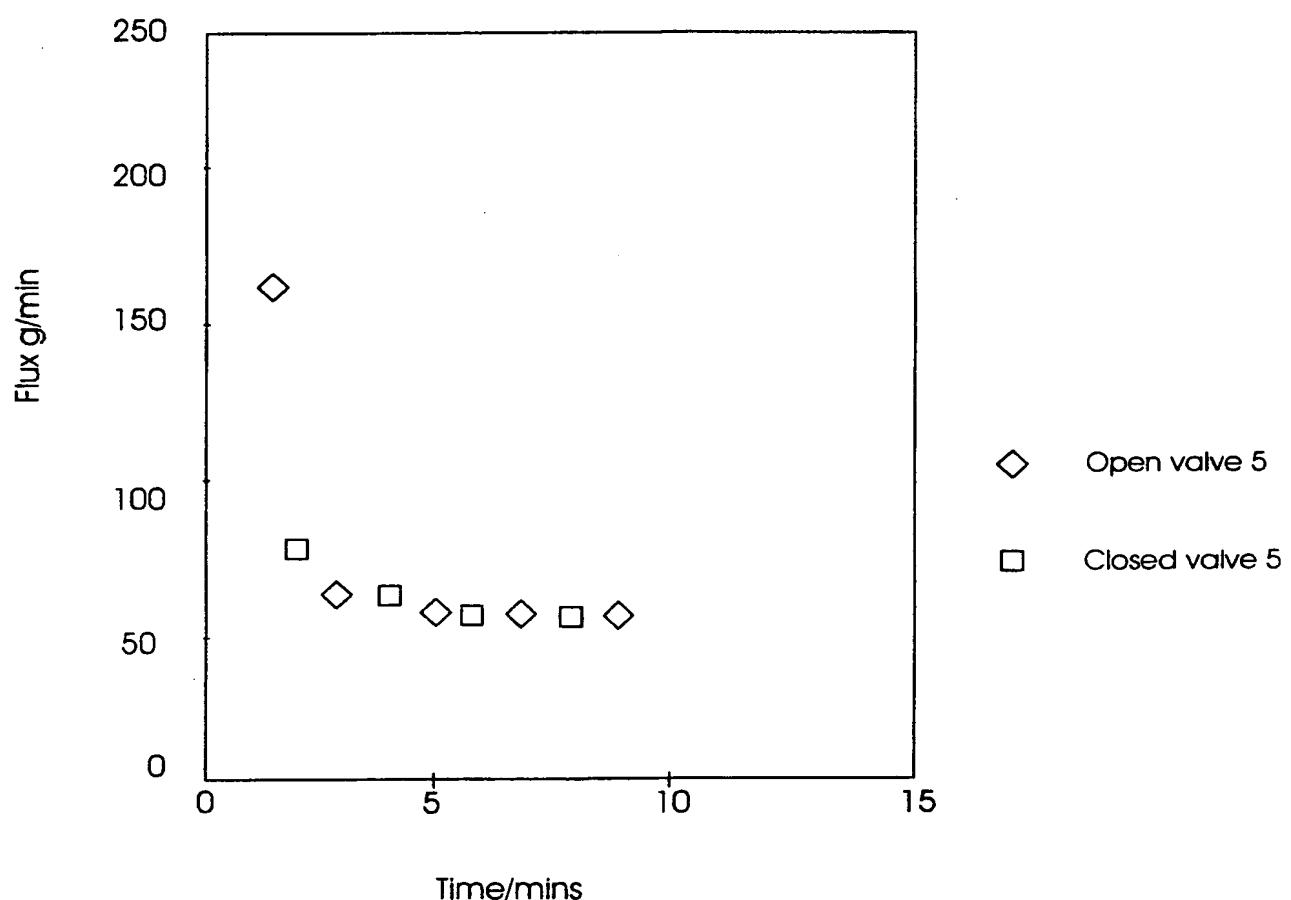


Fig. 4

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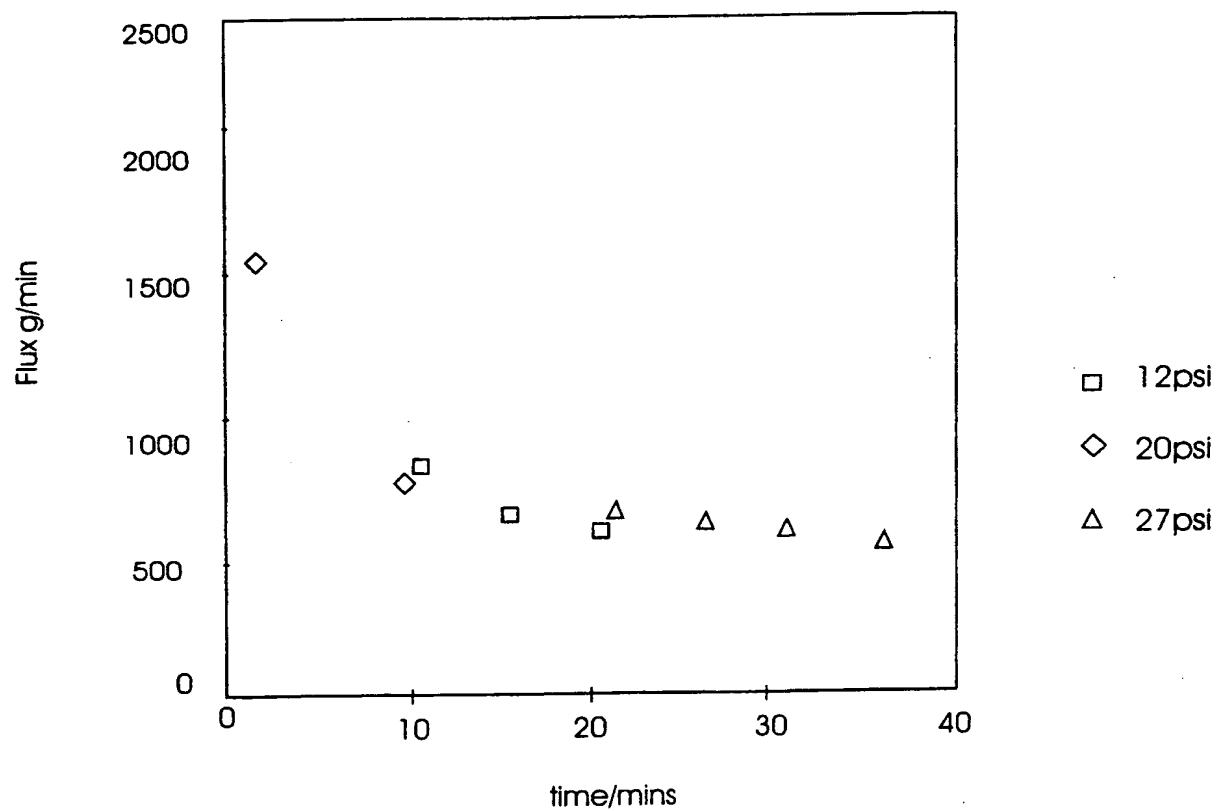


Fig. 5

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International Application No
PCT/GB 99/03312A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01D71/02 B01J37/02 B01D63/06

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IPC 7 B01D B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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